OFFICE OF NAVAL RESEARCH

Contract N00014-92J-1810

R&T CODE: 4133040

TECHNICAL REPORT NO. 8

Electrodeposition of Conductors and Semiconductors with Controlled Stoichiometries and Morphologies.

by

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Prepared for publication

in

Extended Abstracts, Vol. 94-1
The Electrochemical Society
Spring Meeting, San Francisco, May 22-27, 1994

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June 21, 1994

REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	June 21, 1994	Interim

4. TITLE AND SUBTITLE

Electrodeposition of Conductors and Semiconductors with Controlled Stoichiometries and Morphologies

5. FUNDING NUMBERS

Contract # N00014-92J-1810

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

ONR TECHNICAL REPORT #8

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

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13. ABSTRACT (Maximum 200 words)

In an attempt to electrodeposit carbon from CCl_4 in nonaqueous solvents, we observed growth of several unusual morphologies. Fibers with diameters on the order of 0.1-5 microns were synthesized by cathodic galvanostatic electrodeposition from nonaqueous solvents (CH_3CN or CH_2Cl_2) and an electrolyte containing CCl_4 and tetrabutylammonium salts. The fibrous morphology forms without the help of a structural template. Production of fibers can be observed on Ni, Fe, or Cu substrates, with the morphology being very dependent on current density, CCl_4 concentration, and electrode surface preparation. The materials apparently consist of carbon or a carbon nitride compound. The aspect ratio of the fibers ranges from about 2:1 to >100:1, depending upon deposition conditions. Growth of the unusual morphology is presumed to be driven by directional covalent bonding in a graphitic material, analogous to buckminsterfullerene-derived nanotubes.

14. SUBJECT TERMS	15. NUMBER OF PAGES
carbonaceous fibers, electrodeposition, non-aqueous electrochemistry	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

Abstract No. 867

Electrodeposition of Conductors and Semiconductors with Controlled Stoichiometries and Morphologies.

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Experiments directed at the electrochemical synthesis of CdSe, CdTe, carbon, and SiC will be discussed. In an attempt to electrodeposit carbon from CCl_4 in nonaqueous solvents, we observed growth of several unusual morphologies. Fibers with diameters on the order of 0.1-5 microns were synthesized by cathodic galvanostatic electrodeposition from nonaqueous solvents (CH_3CN or CH_2Cl_2) and an electrolyte containing CCl_4 and tetrabutylammonium salts. The fibrous morphology forms without the help of a structural template. Production of fibers can be observed on Ni, Fe, or Cu substrates, with the morphology being very dependent on current density, CCl_4 concentration, and electrode surface preparation. The materials apparently consist of carbon or a carbon nitride compound. The aspect ratio of the fibers ranges from about 2:1 to >100:1, depending upon deposition conditions. Growth of the unusual morphology is presumed to be driven by directional covalent bonding in a graphitic material, analogous to buckminsterfullerene-derived nanotubes.

Preparation

For the semiconductor fibers, working electrodes were cut from 99.5% purity metal foils (Johnson Matthey Electronics). Wires were attached to the backside with conductive Ag paint and the contacts covered with epoxy (Hysol 1C Epoxy Patch Kit). Electrolytic solutions were distilled under nitrogen from the appropriate drying agent, and CCl_4 was vacuum distilled before use. The electrolytic deposition solutions typically consisted of 30 mL of solvent (CH_3CN or CH_2Cl_2), 1 mL of CCl_4, and 1 g of tetrabutylammonium tetrafluoroborate. All electrodeposition experiments were carried out under argon atmosphere. Current density for deposition was typically 3-5 mA/cm^2 and the depositions were carried out for 30-60 min.

Results

Figure 1 shows an electron micrograph of the fibers formed on a Ni substrate, from CH_3CN. The fibers in this image are approximately 5 microns in diameter, and have pronounced striations running parallel to the long axis. The image is not representative of the entire surface. In many places, patches of what appear to be bundles of these fibers are apparent, and in other areas, amorphous chunks of material without any discernible shape are seen.

Figure 2 shows an electron micrograph of fibers formed on a Cu substrate. Coiled structures such as the one in the center of this image were occasionally observed. Many of the fibers that we have observed in this system appear to have more of a square, rectangular, or T-shaped cross section, as opposed to the circular cross sections apparent in figure 1.

The diffuse reflectance infrared spectrum of the material scraped from the electrode surface of several deposition runs (from CH_3CN solutions) displays a sharp, strong absorption band at 2203 cm^{-1}, indicative of an isonitrile species. Presumably this isonitrile is incorporated into the material as a result of CH_3CN solvent decomposition. Separate measurement of the working electrode potential during the course of the depositions showed that it often exceeded the solvent decomposition potential (measured in the absence of CCl_4). However, fiber formation has also been observed in CH_2Cl_2 solution, and so the codecomposition of CH_3CN is not necessary for the production of fibers.

More complete characterization of these materials by X-ray diffraction, X-ray photoelectron, infrared, and Raman spectroscopy, and transmission electron microscopy is in progress.

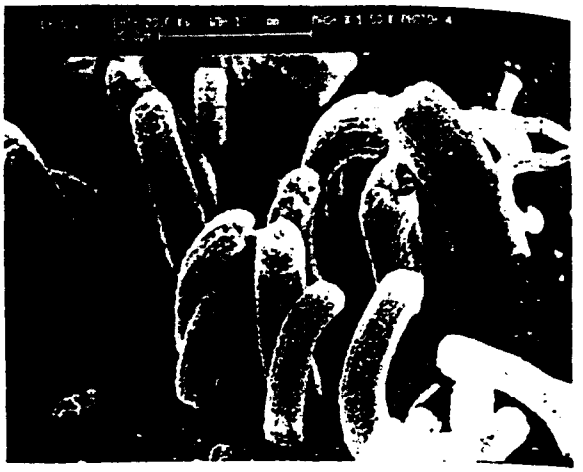

Figure 1: Scanning electron micrograph (secondary electron image, 20 kV) of fibers formed on Ni from cathodic decomposition of CCl_4 in CH_3CN.

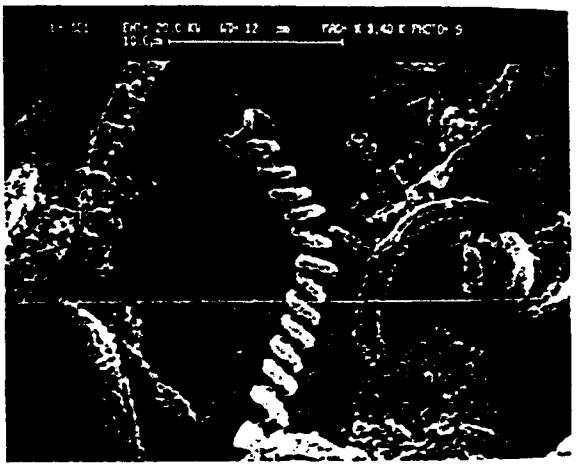

Figure 2: Scanning electron micrograph (secondary electron image, 20 kV) of fibers formed on Cu from cathodic decomposition of CCl_4 in CH_3CN.

Acknowledgment This work was supported by the office of Naval Research.